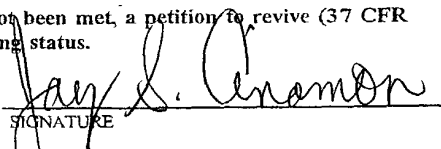


FORM PTO-1396 (REV. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 205,439	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) N/A 10/030241	
INTERNATIONAL APPLICATION NO. PCT/EP/00/05724		INTERNATIONAL FILING DATE June 21, 2000		PRIORITY DATE CLAIMED June 25, 1999	
TITLE OF INVENTION USE OF PHOTOCATALYTIC PREPARATIONS OF COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING THE ORIGINAL APPEARANCE OF CEMENTITIOUS, STONE, OR MARBLE PRODUCTS.					
APPLICANT(S) FOR DO/EO/US Rossano AMADELLI; Luigi CASSAR; Carmine PEPE					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <b>unsigned</b></p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11 to 20 below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input type="checkbox"/> Other items or information:</p>					

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>10/030241</b>		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
21. <input type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>          	
				\$ 890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	43 - 20 =	23	x \$18.00	\$ 414.00	
Independent claims	3 - 3 =	0	x \$84.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
<b>SUBTOTAL =</b>				\$ 1,304.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				\$ 1,304.00	
				Amount to be refunded:	\$
				charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1,304.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-0035</u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:  ABELMAN FRAYNE & SCHWAB Attorney at Law 150 East 42nd Street New York, NY 10017  (212) 949-9022					
				SIGNATURE  NAME Jay S. Cinamon 24,156 REGISTRATION NUMBER December 21, 2001	

PATENT DOCKET 205,439

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: AMADELLI ET AL. EXAMINER:  
SERIAL NO.: 10/030,241 ART UNIT.:  
FILED: December 21, 2001  
TITLE: USE OF PHOTOCATALYTIC  
PREPARATIONS OF COLLOIDAL  
TITANIUM DIOXIDE FOR  
PRESERVING THE ORIGINAL  
APPEARANCE OF CEMENTITIOUS,  
STONE, OR MARBLE PRODUCTS

April 11, 2002

PRE-EXAMINATION AMENDMENT

Hon. Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

SIR:

STATEMENT OF FILING BY EXPRESS MAIL 37 C.F.R. § 1.10

This correspondence is being deposited with the United States Postal Service on April 11, 2002 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number ET 537 596 911 US addressed to the Honorable Commissioner for Patents, Washington, D.C. 20231.

Please amend the application prior to proceeding with its examination.

IN THE CLAIMS

Please amend claim 74 as follows:

74. (Amended) A method according to claim 62, for the oxidation of nitrogen oxides (NO<sub>x</sub>).

IN THE TITLE

Please delete the word "cementitiuos" and replace it with --cementitious--.

The title should read:

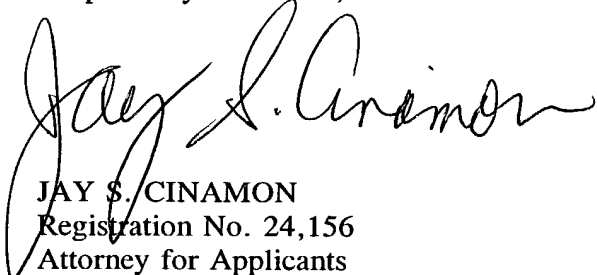
"USE OF PHOTOCATALYTIC PREPARATIONS OF COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING THE ORIGINAL APPEARANCE OF CEMENTITIOUS, STONE, OR MARBLE PRODUCTS"

REMARKS

It is respectfully requested that the examination of this application proceed on the basis of the amendatory action taken herein and that this amendment be entered.

Attached is a Marked-Up Version Showing Changes Made by this Pre-Examination  
Amendment.

Respectfully submitted,



JAY S. CINAMON  
Registration No. 24,156  
Attorney for Applicants

**ABELMAN FRAYNE & SCHWAB**  
150 East 42nd Street  
New York, New York 10017-5612  
Tel. (212) 949-9022  
Fax (212) 949-9190

Docket No.: 205,439MARKED-UP VERSION SHOWING CHANGES MADEIN THE CLAIMS

Claim 74 has been amended as follows:

74. (Amended) A method according to claim 74 62, for the oxidation of nitrogen oxides (NO<sub>x</sub>).

IN THE TITLE

The word "cementitiuos" has been replaced with --cementitious--.

The title should read:

"USE OF PHOTOCATALYTIC PREPARATIONS OF COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING THE ORIGINAL APPEARANCE OF CEMENTITIUS CEMENTITIOUS, STONE, OR MARBLE PRODUCTS"

notarbar\41102ama.px

PATENT DOCKET 205,439

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICANT: AMADELLI et al. EXAMINER: N/A  
SERIAL NO.: Not yet assigned ART UNIT: N/A  
FILED: Not yet assigned  
TITLE: USE OF PHOTOCATALYTIC PREPARATIONS OF  
COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING  
THE ORIGINAL APPEARANCE OF CEMENTITIUS,  
STONE OR MARBLE PRODUCTS.

DATE: December 21, 2001

**PRELIMINARY AMENDMENT**

Hon. Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

SIR:

**STATEMENT OF FILING BY EXPRESS MAIL 37 C.F.R. § 1.10**

This correspondence is being deposited with the United States Postal Service on  
December 21, 2001 in an envelope as "Express Mail Post Office to Addressee" Mailing Label  
Number ET 537 596 182 US addressed to the Honorable Commissioner for Patents and  
Trademarks, Washington, DC 20231.

Please amend the application filed on even date herewith prior to proceeding with this examination.

**IN THE CLAIMS**

Please cancel claims 1-61, inclusive, without prejudice or disclaimer.

Please add new claims 62-105, inclusive, as follows:

-- 62. A method for preserving the original appearance of cementitious, stone, or marble product from the action of atmospheric agents, characterized in that the surfaces of said products are treated with colorless colloidal preparations of titanium dioxide or one of its precursors.

63. A method according to Claim 62, wherein in which the preparations of titanium dioxide or one of its precursors contain a metal ion chosen from the groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.

64. A method according to Claim 63, wherein the preparations of titanium dioxide or one of its precursors contain a metal ion selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.

65. A method according to Claim 64, wherein the preparations of titanium dioxide or one of its precursors contain ions selected from the group consisting of magnesium, cerium, niobium, and lanthanum.



66. A method according to Claim 63, wherein the preparations of titanium dioxide or one of its precursors contain the metal ion in an amount of from 0.1 to 5% (percentage expressed as metal-ion atoms with respect to the titanium atoms).

67. A method according to Claim 66, wherein the preparations of titanium dioxide or one of its precursors contain the metal ion in an amount of from 0.1 to 1%.

68. A method according to Claim 62, wherein the titanium dioxide is prevalently in the form of anatase.

69. A method according to Claim 68, wherein at least 75% of titanium dioxide is in the form of anatase.

70. A method according to Claim 62, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.

71. A method according to Claim 70, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.

72. A method according to Claim 70, wherein the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium alkoxide.

73. A method according to Claim 62, for the oxidation of polluting substances chosen from the group comprising organic substances present in the environment as a result of motor-vehicle exhaust or industrial emissions, and inorganic compounds.

74. A method according to Claim 74, for the oxidation of nitrogen oxides ( $\text{NO}_x$ ).

75. A method according to Claim 62, wherein the titanium dioxide in colloidal form is prepared using sol-gel techniques so as to obtain particles having a size of between 10 and 200 Å.

76. A method according to Claim 75, wherein the particles of titanium dioxide have a size of between 50 and 100 Å.

77. A method according to Claim 62, wherein an aqueous suspension of the colloidal preparation of titanium dioxide or one of its precursors is applied on the product in small successive amounts until the desired thickness is reached.

78. A method according to Claim 77, wherein the colloidal preparation is vacuum-dried so as to obtain a powder which can be re-suspended in water, maintaining its colloidal properties.

79. A cementitious, stone, or marble product, characterized in that it is coated with a colloidal preparation of titanium dioxide or one of its precursors.

80. A cementitious, stone, or marble product according to Claim 79, wherein a preparation of titanium dioxide or one of its precursors contains a metal ion chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.

81. A cementitious, stone, or marble product according to Claim 80, wherein a preparation of titanium dioxide or one of its precursors contains a metal ion selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.

82. A cementitious, stone, or marble product according to Claim 81, wherein a preparation of titanium dioxide or one of its precursors contains ions selected from the group consisting of magnesium, cerium, niobium, and lanthanum.

83. A cementitious, stone, or marble product according to Claim 80, wherein a preparation of titanium dioxide or one of its precursors contains the metal ion in an amount of from 0.1 to 5% (percentage expressed as metal-ion atoms with respect to the titanium atoms).

84. A cementitious, stone, or marble product according to Claim 83, wherein a preparation of titanium dioxide or one of its precursors contains the metal ion in an amount of from 0.1 to 1%.

85. A cementitious, stone, or marble product according to Claim 62, wherein the titanium dioxide is prevalently in the form of anatase.

86. A cementitious, stone, or marble product according to Claim 68, wherein at least 75% of titanium dioxide is in the form of anatase.

87. A cementitious, stone, or marble product according to Claim 62, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.

88. A cementitious, stone, or marble product according to Claim 87, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.

89. A cementitious, stone, or marble product according to Claim 70, wherein the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium alkoxide.

90. A cementitious, stone, or marble product according to Claim 62, wherein a preparation of titanium dioxide or one of its precursors has the function of oxidant for polluting substances chosen from the group comprising organic substances present in the environment as a result of motor-vehicle exhaust or industrial emissions, and inorganic compounds.

91. A cementitious, stone, or marble product according to Claim 90, wherein a preparation of titanium dioxide or one of its precursors has the function of oxidant for nitrogen oxides ( $\text{NO}_x$ ).

92. A cementitious, stone, or marble product according to Claim 62, wherein the titanium dioxide in colloidal form is prepared using sol-gel techniques so as to obtain particles having a size of between 10 and 200 Å.

93. A cementitious, stone, or marble product according to Claim 75, wherein the particles of titanium dioxide have a size of between 50 and 100 Å.

94. A cementitious, stone, or marble product according to Claim 62, wherein an aqueous suspension of the colloidal preparation of titanium dioxide or one of its precursors is applied on the product in small successive amounts until the desired thickness is reached.

95. A cementitious, stone or marble product according to Claim 62, wherein the colloidal suspension of titanium dioxide or one of its precursors is vacuum-dried so as to obtain a powder which can be re-suspended in water, maintaining its colloidal properties.

96. A process for the creation of colorless colloidal preparations of titanium dioxide or of one to its precursors containing a metal ion chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof, characterized in that the hydrolysis of the titanium dioxide precursors takes place directly in the presence of the salt of the metal ion

by co-precipitation or mixing and characterized in that the metal ion is present in an amount of from 0.1 to 5% (percentage expressed as metal-ion atoms with respect to the titanium atoms).

97. A process according to Claim 96, wherein the metal ion is chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.

98. A process according to Claim 97, wherein the metal ion is selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.

99. A process according to Claim 98, wherein the ions are selected from the group consisting of magnesium, cerium, niobium, and lanthanum.

100. A process according to Claim 96, wherein the metal ion is present in an amount of from 0.1 to 1%.

101. A process according to Claim 96, wherein the titanium dioxide is prevalently in the form of anatase.

102. A process according to Claim 101, wherein at least 75% of titanium dioxide is in the form of anatase.

103. A process according to Claim 96, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.

104. A process according to Claim 103, wherein the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.

105. A process according to Claim 86, wherein the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium alkoxide. --

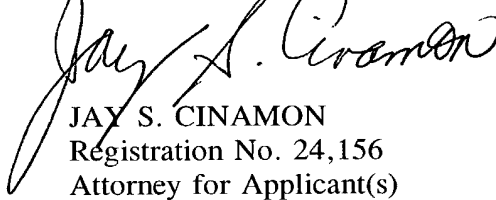
**REMARKS**

It is respectfully requested that the examination that this application proceed on the basis of the amendatory action taken herein and that this amendment be entered prior to calculating the filing fee and according the application a filing date.

It is respectfully submitted that claims 62-105, inclusive, are in condition for allowance, and a Notice of Allowance to that effect is respectfully requested.

Please charge any fees which may be due and have not been submitted herewith to our deposit account no. 01-0035.

Respectfully submitted,



JAY S. CINAMON  
Registration No. 24,156  
Attorney for Applicant(s)

**ABELMAN FRAYNE & SCHWAB**  
150 East 42nd Street  
New York, New York 10017-5612  
Tel. (212) 949-9022  
Fax (212) 949-9190

x222\amadelll.amd

USE OF PHOTOCATALYTIC PREPARATIONS OF COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING THE ORIGINAL APPEARANCE OF CEMENTITIOUS, STONE, OR MARBLE PRODUCTS.

Field Of The Invention

- 5 The present invention refers to the use of colloidal photocatalytic preparations of titanium dioxide ( $\text{TiO}_2$ ) for maintaining the original appearance of cementitious, stone, or marble products.

Prior Art

- 10 The conservation of architectural assets depends to a considerable extent on the environment in which they are located. The problem of the preservation of such assets assumes important dimensions if it is considered that the action of atmospheric agents has become increasingly aggressive over time.

- 15 The conservation of architectural structures, buildings and artefacts subject to outdoor exposure has to do with forces that act in an important way on the surface of the constructions or in the layers immediately below the surface and that regard the depositing of organic and inorganic materials which usually adhere to the aforesaid organic substrate, and the action of acid rain.

- 20 One of the main problems of architectural cementitious, stone, or marble products therefore regards the constant maintenance over time of their original appearance, which is undermined by the natural process of ageing due to the influence of atmospheric agents.

The need is therefore particularly felt for economical systems of intervention which enable conservation of the aesthetic characteristics of the surface of constructions made of cementitious, stone, or marble material.

- 25 With the aim of protecting such artefacts, various techniques are resorted to, the most common of which consist in applying water-repellent products, such as silicone solutions that are stable in alkaline environments and are stable to light and weather. Unfortunately, the progressive increase in the pollutants present in a typical metropolitan environment, perhaps also on account of their frequently  
30 acidic nature, has markedly limited the duration of this type of protection, with consequent aesthetic degradation of the artefact.

In order to overcome this new problem, various solutions have been proposed. For

example, the patent IT 1286492 (in the name of the present applicant) illustrates a hydraulic binder for cementitious compositions which comprises in its mass a titanium-dioxide based photocatalyst that is able to oxidize, and hence neutralize, the polluting substances present in the environment. This type of solution is certainly valid as regards the protection of the surface of the artefact from any possible deterioration caused, for example, by wind abrasion, but clearly it implies the use of enormous amounts of photocatalyst as compared to those actually needed. In fact, the photocatalyst is present not only on the surface of the artefact or in the immediately underlying layers, i.e., in the areas where its presence proves useful, but in the entire cementitious mass, which, for the most part, will never come into contact with external agents.

Alternative solutions have also been proposed (see, for example, the European patent application No. EP 0 885 857 in the name of the present applicant) which regard cementitious levelling plasters containing various polymeric additives and photocatalysts that are able to oxidize the polluting substances present in the environment, but these cementitious-based formulations are white, and cannot be used, for instance, on marble or stone materials without consequently modifying their aesthetic characteristics.

The use of anatase, which is one of the tetragonal crystalline forms of titanium dioxide, as photocatalyst for the oxidation of organic pollutants has been known for some time, also in the form of colloidal preparations.

The patent EP 784034 (in the name of Matsushita Electric Works) describes substrates obtained by depositing titanium dioxide on the surface of a substrate by deposition of a solution containing ammonium titanium fluoride, followed by calcining. The patent EP 614682 (in the name of Fuji Electric) illustrates a titanium-based or titanium/activated carbon-based photocatalyst fixed on a fluororesin to obtain sheets or panels to be applied externally on buildings for removing low concentrations of  $\text{NO}_x$ .

The incorporation of metal ions (doping agents) in these preparations alters the photocatalytic activity of titanium dioxide to a substantial extent. The most important parameters are the type of ion, the concentration of the dopants, and the thermal treatment useful for the formation of the photocatalyst.



Brezová V. *et al.*, J. Photochem. Photobiol. A: Chem., 109, (1997), 177-183, analyze the influence of various metal ions and their concentrations in a particular application of titanium dioxide as photocatalyst, namely, in the oxidation of phenol. In particular, preparations of colloidal titanium dioxide are described, in which the titanium dioxide is doped with various metals at 5 % atom/atom, following a procedure whereby colloidal titanium dioxide is first prepared, and next the salt of the doping metal is mixed under heating. Among the various metal ions tested, cerium is reported to reduce the photocatalytic activity of the colloidal titanium dioxide. In the publication, as in other previous publications on this subject, no mention is made of the use of the said photocatalytic products on cementitious materials.

The patent EP 633964 (in the name of Fujisawa, Hashimoto, and Ishihara Sangyo Kaisha) describes a  $\text{TiO}_2$ -based photocatalyst preferably doped with V, Fe, Cu, Co, Ni, Zn, Ru, Rh, Pd, Ag, Pt, or Au, and fixed on a fluorinated polymer for adhesion to the substrate. This photocatalyst is useful for purifying air, but also water, from various undesired substances.

#### Summary Of The Invention

It has now been surprisingly found that colourless colloidal preparations of titanium dioxide, or of one of its precursors, possibly doped with elements chosen from groups I-VA, and the lanthanide and actinide series of the periodic table, or mixtures thereof, preferably magnesium, cerium, niobium or lanthanum, when applied on the surface of cementitious, stone, or marble products, are able to preserve the original appearance of the surface, without altering the characteristics of the cementitious, stone, or marble material.

The solution devised thus regards a system for treating cementitious, stone, or marble surfaces by using titanium dioxide-based colourless colloidal suspensions, the titanium dioxide being possibly doped with elements chosen from groups I-VA, and the lanthanide and actinide series of the periodic table.

#### Detailed Description Of The Invention

The present invention refers to the use of colourless colloidal preparations of titanium dioxide or one of its precursors, for the conservation of the original appearance of cementitious, stone, and marble products, by means of application

By cementitious artefact is meant any product in the hardened state deriving from a cementitious composition or cementitious mixture, by cementitious composition or cementitious mixture being meant any composition in which the binder is mixed with water and possibly with aggregates of various grain size. The cementitious compositions thus include both cementitious pastes, i.e., pastes consisting of



UV and visible-light measurements using diffused-reflectance spectroscopy reveal the minimum quantity suitable for guaranteeing maximum light absorption by the  $\text{TiO}_2$ .

As an alternative, the colloidal suspension can be vacuum-dried in order to obtain a titanium-dioxide powder which can be preserved for an unlimited period and re-suspended in water, maintaining its colloidal properties.

When applied on the surface of cementitious, stone, or marble products, the colloidal preparations according to the present invention effectively protect the product from alterations due to organic pollutants, and in general from atmospheric agents, by causing their photo-oxidation.

Generally, when inorganic pollutants do not find an organic substrate to adhere to, they encounter greater difficulties in depositing on the surface of the product.

As compared to the methods of the prior art, the application of the preparations in question guarantees a form of protection of the above-mentioned products that is long-lasting by using amounts of material, namely titanium dioxide or one of its precursors, that are considerably smaller than those required by the methods described previously.

In particular, the effectiveness of the titanium dioxide according to the present invention, possibly doped with metal ions belonging to groups I-VA, and the lanthanide or actinide series of the periodic table, as compared to the use of other formulations of titanium dioxide, considerably accelerates photo-oxidation of polluting agents, as illustrated in the assays described later (Examples 9, 10 and 11).

Particularly surprising is the fact that the colloidal titanium dioxide prepared according to the present invention reveals excellent adhesion to the cementitious, marble or stone material to be protected.

This was verified by subjecting specimens of cementitious and marble material treated with the titanium-dioxide colloidal suspension to leaching in water under stirring (Examples 7 and 8).

It is to be noted that the colloid according to the present invention finds in cementitious, marble or stone materials an optimal substrate for the photocatalytic action envisaged, whilst for other materials, such as glass, adhesion of the colloid

### EXAMPLE 4

Preparation of colloidal titanium dioxide doped with magnesium

Using magnesium (II) chloride hexahydrate (0.0213 g) to be dissolved in the hydrolysis water (150 ml), and titanium isopropoxide (25 ml), and following the procedure described in Example 1, the product in question, containing 0.1%  $Mg^{2+}$ ,  
 5 was obtained.

EXAMPLE 5

Preparation of colloidal titanium dioxide doped with lanthanum

Using lanthanum (III) nitrate hexahydrate (0.037 g) to be dissolved in the hydrolysis water (150 ml), and titanium isopropoxide (25 ml), and following the  
 10 procedure described in Example 1, the product in question, containing 0.1%  $La^{3+}$ , was obtained.

EXAMPLE 6

Preparation of colloidal films on glass substrates

The colloid (10 ml) prepared as described in Examples 1-5 was put in a  
 15 hermetically sealed glass container so as to hinder complete evaporation of the water and at the same time favour the regular growth of the particles from an average size of 50 Å to a maximum size of 100/200 Å, and was then heated up to 200-220°C overnight. The precipitated colloid was re-suspended by mechanical stirring and vacuum heat-concentrated until a concentration of 150 g/l was  
 20 obtained. Next, Carbowax 2000 (300 mg) was added, and the dispersion underwent stirring for 8 hours until total dissolution of the Carbowax was achieved and a homogeneous suspension was obtained.

The resulting product was spread on glass substrates and set to dry in a muffle oven at 500°C for 30 minutes. The film was characterized by means of diffused-  
 25 reflectance spectroscopy.

Without the use of the Carbowax crosslinking agent it is impossible to get the colloid to adhere to a glass substrate.

EXAMPLE 7

Preparation of colloidal films on cementitious-mortar substrates

30 The colloid (10 ml) prepared as described in Examples 1-5 was put in a hermetically sealed glass container so as to hinder complete evaporation of the water and at the same time favour the regular growth of the particles from an

average size of 50 Å to a maximum size of 100/200 Å, and was then heated up to 200-220°C overnight.

Specimens of cementitious mortar (disks sized 25x8x2.5 cm) were prepared using white cement Italbiano Italcementi 52.5 R.

- 5 After the preparation, the specimens were cured for 1 day in moulds in an environment at 20°C and relative humidity (RH) > 90%. After ejection, the specimens were kept for a further 7 days at 20°C and RH ≈ 60%.

The aqueous suspension was brush-applied on the said specimens of cementitious mortar.

- 10 The colloid was brush-applied in small successive amounts until the typical spectrum observed in diffused-reflectance spectroscopy was obtained. Leaching tests were carried out in water for 48 hours, under stirring, and these tests confirmed the adhesion of the colloid. Each test specimen was then observed in diffracted-reflectance spectroscopy. In all, the equivalent in weight of  
15 approximately 1g/m<sup>2</sup> was applied on each test specimen.

#### EXAMPLE 8

##### Preparation of colloidal films on marble substrates

- The colloid (10 ml) prepared as described in Examples 1-5 was put in a hermetically sealed glass container so as to hinder complete evaporation of the  
20 water and at the same time favour the regular growth of the particles from an average size of 50 Å to a maximum size of 100/200 Å, and was then heated up to 200-220°C overnight.

- The colloidal suspension was vacuum-dried so as to obtain a titanium-dioxide powder, which was re-suspended in water (4-5 g/l) and brush-applied on a  
25 specimen of white Carrara marble (dimensions, 3x3x3 cm). Leaching tests were carried out in water for 48 hours, under stirring, and these tests confirmed the adhesion of the colloid. Each test specimen was then observed in diffracted-reflectance spectroscopy. An amount of titanium dioxide corresponding in weight to approximately 1 g/m<sup>2</sup> was evaluated.

#### 30 EXAMPLE 9

##### Degradation of 4-chlorophenol

4-chlorophenol 10 mM (3 ml) was put in an irradiation cell, in which each time

were suspended the specimens prepared according to Example 7 with the colloids prepared according to Examples 1-4 and containing the catalysts according to the invention, and, as a standard specimen for comparison, a specimen prepared in a similar way using Degussa titanium dioxide, which, to the knowledge of the present applicant, is the most active photo-oxidation catalyst present on the market. The cell was closed under oxygen, and the degradation of the 4-chlorophenol was monitored by spectrophotometry, measuring the degradation times (in hours). The results are given in Figure 1 below.

Figure 1

10	Coll. $\text{TiO}_2$ + Mg
	Coll. $\text{TiO}_2$ + Nb
	Coll. $\text{TiO}_2$ + Ce
	Coll. $\text{TiO}_2$
	Degussa $\text{TiO}_2$
15	Degradation time (hours)

As may be seen in Figure 1, the specimens containing the dopant ions yield a time of degradation of the pollutant lower both with respect to the test specimen containing colloidal titanium dioxide and with respect to the standard specimen containing Degussa titanium dioxide.

#### EXAMPLE 10

##### Degradation of naphthionic acid

Following basically the procedure described in Example 9, but performing the decomposition of naphthionic acid 0.026 mM (3 ml) in water, an evaluation was made of the behaviour of the specimen prepared according to Example 7, using the titanium-dioxide colloid doped with lanthanum according to classic methods and prepared as described in Example 5. For comparison, two non-colloidal standard specimens of Degussa titanium dioxide were evaluated, one as such, and the other doped with lanthanum according to classic methods. The results are given in Figure 2 below.

Figure 2

Coll.  $\text{TiO}_2$  + La



Coll. TiO<sub>2</sub>

Degussa TiO<sub>2</sub> + La 1%

Degussa TiO<sub>2</sub>

5 Degradation time (minutes)

As may be seen in Figure 2, the degradation time for the colloidal titanium dioxide is lower than for the Degussa titanium dioxide, both in the case of the specimen containing the dopant ion and in the case of the specimen not containing the  
10 dopant ion.

#### EXAMPLE 11

##### Degradation of 3-4-dihydroxycinnamic acid

Following basically the procedure described in Example 9, and using 3-4-dihydroxycinnamic acid 0.26 mM (3 ml) in water, the following were evaluated:

- 15 a) behaviour of the specimen prepared according to Example 7, using the titanium-dioxide colloid doped with niobium prepared as described in Example 3;
- b) behaviour of the specimen prepared according to Example 7, using the titanium-dioxide colloid doped with magnesium prepared as described in Example 4; and
- 20 c) behaviour of the specimen of colloidal titanium dioxide prepared according to Example 8 on a marble test specimen.

For comparison, a standard specimen of Degussa non-colloidal titanium dioxide was evaluated. The results are illustrated in Figure 3.

#### Figure 3

25 Coll. TiO<sub>2</sub> + Mg

Coll. TiO<sub>2</sub> + Nb

Coll. TiO<sub>2</sub> on marble

Coll. TiO<sub>2</sub> on mortar

Degussa TiO<sub>2</sub>

30 Decolorizing time (minutes)

As may be seen in Figure 3, the decolorizing times (oxidation of the pollutant) of

the photocatalysts according to the present invention are in all cases shorter than for the Degussa titanium dioxide in the non-colloidal form.

## EXAMPLE 12

### Degradation of alcoholic extract of tobacco

- 5 Following basically the procedure described in Example 9, and using alcoholic extract of tobacco on cement matrices, the following were evaluated:
- a) behaviour of the specimen prepared according to Example 7, using the titanium-dioxide colloid described in Example 1;
  - b) behaviour of the specimen prepared according to Example 7, using the
  - 10 titanium-dioxide colloid doped with cerium prepared as described in Example 2; and
  - c) behaviour of the specimen prepared according to Example 7, using the titanium-dioxide colloid doped with magnesium as described in Example 4.

The alcoholic extract of tobacco was added in an amount such as to produce a

15 drop in transmittance from 75 to 40, read at 450 nm.

For comparison, Degussa titanium dioxide standard specimens, one at 10% and one at 0.1%, were evaluated. The results are illustrated in Figure 4.

Figure 4

	Coll. TiO <sub>2</sub> + Mg
20	Coll. TiO <sub>2</sub> + Ce
	Coll. TiO <sub>2</sub> + Nb
	Coll. TiO <sub>2</sub>
	Degussa TiO <sub>2</sub> , 10%
	Degussa TiO <sub>2</sub> , 0.1%
25	Degradation time (hours)

As may be seen in Figure 4, the times of degradation of the pollutant for the photocatalysts according to the present invention are in all cases shorter than for the Degussa titanium dioxide in the non-colloidal form.

## CLAIMS

1. Use of colourless colloidal preparations of titanium dioxide or of one to its precursors, for the conservation of the original appearance of cementitious, stone, or marble products, by the application of said preparations on the surfaces of the above-mentioned products.
2. Use of preparations according to Claim 1 containing a metal ion chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.
3. Use of preparations according to Claim 2 containing a metal ion selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.
4. Use of preparations according to Claim 3 containing ions selected from the group consisting of magnesium, cerium, niobium, and lanthanum.
5. Use of preparations according to Claim 2 containing the metal ion in an amount of from 0.1 to 5% (percentage expressed as metal-ion atoms with respect to the titanium atoms).
6. Use of preparations according to Claim 5 containing the metal ion in an amount of from 0.1 to 1%.
7. Use of preparations according to Claim 1 in which the titanium dioxide is prevalently in the form of anatase.
8. Use of preparations according to Claim 7 in which at least 75% of titanium dioxide is in the form of anatase.
9. Use of preparations according to Claim 1 in which the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.
10. Use of preparations according to Claim 9 in which the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.
11. Use of preparations according to Claim 9 in which the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium alkoxide.
12. Use of preparations according to Claim 1 for the oxidation of polluting

substances chosen from the group comprising organic substances present in the environment as a result of motor-vehicle exhaust or industrial emissions, and inorganic compounds.

- 5 13. Use of preparations according to Claim 12 for the oxidation of nitrogen oxides ( $\text{NO}_x$ ).
14. Use of preparations according to Claim 1 in which the titanium dioxide in colloidal form is prepared using sol-gel techniques so as to obtain particles having a size of between 10 and 200 Å.
- 10 15. Use of preparations according to Claim 14 in which the particles of titanium dioxide have a size of between 50 and 100 Å.
16. Use of preparations according to Claim 1 in an aqueous suspension which is applied on the product in small successive amounts until the desired thickness is reached.
- 15 17. Use of preparations according to Claim 1 in which the colloidal suspension is vacuum-dried so as to obtain a powder which can be re-suspended in water, maintaining its colloidal properties.
18. A method for preserving the original appearance of cementitious, stone, or marble product from the action of atmospheric agents, characterized in that the surfaces of said products are treated with colourless colloidal preparations of
- 20 titanium dioxide or one of its precursors.
19. A method according to Claim 18, in which the preparations of titanium dioxide or one of its precursors contain a metal ion chosen from the groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.
- 25 20. A method according to Claim 19, in which the preparations of titanium dioxide or one of its precursors contain a metal ion selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.
21. A method according to Claim 20, in which the preparations of titanium dioxide or one of its precursors contain ions selected from the group consisting of
- 30 magnesium, cerium, niobium, and lanthanum.
22. A method according to Claim 19, in which the preparations of titanium dioxide or one of its precursors contain the metal ion in an amount of from 0.1 to 5%

(percentage expressed as metal-ion atoms with respect to the titanium atoms).

23.A method according to Claim 22, in which the preparations of titanium dioxide or one of its precursors contain the metal ion in an amount of from 0.1 to 1%.

24.A method according to Claim 18, in which the titanium dioxide is prevalently in the form of anatase.

25.A method according to Claim 24, in which at least 75% of titanium dioxide is in the form of anatase.

26.A method according to Claim 18, in which the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.

27.A method according to Claim 26, in which the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.

28.A method according to Claim 26, in which the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium alkoxide.

29.A method according to Claim 18, for the oxidation of polluting substances chosen from the group comprising organic substances present in the environment as a result of motor-vehicle exhaust or industrial emissions, and inorganic compounds.

30.A method according to Claim 29, for the oxidation of nitrogen oxides ( $\text{NO}_x$ ).

31.A method according to Claim 18, in which the titanium dioxide in colloidal form is prepared using sol-gel techniques so as to obtain particles having a size of between 10 and 200 Å.

32.A method according to Claim 32, in which the particles of titanium dioxide have a size of between 50 and 100 Å.

33.A method according to Claim 18, in which an aqueous suspension of the colloidal preparation of titanium dioxide or one of its precursors is applied on the product in small successive amounts until the desired thickness is reached.

34.A method according to Claim 33, in which the colloidal preparation is vacuum-dried so as to obtain a powder which can be re-suspended in water, maintaining its colloidal properties.

35.A cementitious, stone, or marble product, characterized in that it is coated with a colloidal preparation of titanium dioxide or one of its precursors.

46. A cementitious, stone, or marble product according to Claim 35, in which a preparation of titanium dioxide or one of its precursors has the function of oxidant for polluting substances chosen from the group comprising organic substances present in the environment as a result of motor-vehicle exhaust or industrial emissions, and inorganic compounds.
47. A cementitious, stone, or marble product according to Claim 46, in which a preparation of titanium dioxide or one of its precursors has the function of oxidant for nitrogen oxides ( $\text{NO}_x$ ).
48. A cementitious, stone, or marble product according to Claim 35, in which the titanium dioxide in colloidal form is prepared using sol-gel techniques so as to obtain particles having a size of between 10 and 200 Å.
49. A cementitious, stone, or marble product according to Claim 48, in which the particles of titanium dioxide have a size of between 50 and 100 Å.
50. A cementitious, stone, or marble product according to Claim 35, in which an aqueous suspension of the colloidal preparation of titanium dioxide or one of its precursors is applied on the product in small successive amounts until the desired thickness is reached.
51. A cementitious, stone or marble product according to Claim 35, in which the colloidal suspension of titanium dioxide or one of its precursors is vacuum-dried so as to obtain a powder which can be re-suspended in water, maintaining its colloidal properties.
52. A process for the creation of colourless colloidal preparations of titanium dioxide or of one to its precursors containing a metal ion chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof, characterized in that the hydrolysis of the titanium dioxide precursors takes place directly in the presence of the salt of the metal ion by co-precipitation or mixing and characterized in that the metal ion is present in an amount of from 0.1 to 5% (percentage expressed as metal-ion atoms with respect to the titanium atoms).
53. A process according to Claim 52, characterized in that the metal ion is chosen from groups I-VA, and the lanthanide or actinide series of the periodic table, and mixtures thereof.

54. A process according to Claim 53, characterized in that the metal ion is selected from the group consisting of lithium, beryllium, magnesium, scandium, yttrium, lanthanum, cerium, niobium, vanadium, zirconium, and mixtures thereof.
55. A process according to Claim 54, characterized in that the ions are selected  
5 from the group consisting of magnesium, cerium, niobium, and lanthanum.
56. A process according to Claim 52, characterized in that the metal ion is present in an amount of from 0.1 to 1%.
57. A process according to Claim 52, characterized in that the titanium dioxide is prevalently in the form of anatase.
- 10 58. A process according to Claim 57, characterized in that at least 75% of titanium dioxide is in the form of anatase.
59. A process according to Claim 52, characterized in that the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase.
- 15 60. A process according to Claim 59, characterized in that the titanium-dioxide precursor is a product able to produce titanium dioxide prevalently in the form of anatase with appropriate types of thermal treatment.
61. A process according to Claim 59, characterized in that the titanium-dioxide precursor is chosen from the group comprising  $\text{TiCl}_4$ ,  $\text{TiOSO}_4$ , and titanium  
20 alkoxide.

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- (71) Applicant (for all designated States except US): ITAL-CEMENTI S.P.A. [IT/IT]; Via Camozzi, 124, I-24121 Bergamo (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): AMADELLI, Rossano [IT/IT]; Via Massarenti, 39 - Fraz. Gualdo, I-44019 Voghiera (IT). CASSAR, Luigi [IT/IT]; Via Europa, 42, I-20122 S. Donato Milanese (IT). PEPE, Carmine [IT/IT]; Via Casnidelli, 12, I-24010 Ponteranica (IT).
- (74) Agent: GERVASI, Gemma; Notarbartolo & Gervasi S.p.A., Corso di Porta Vittoria, 9, I-20122 Milano (IT).
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(57) Abstract: Use of photocatalytic preparations of colloidal titanium dioxide optionally doped with a metal chosen from groups I-VA, and the lanthanide and actinide series of the periodic table, for preserving the original appearance of cementitious, stone, and marble products.

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# UNITED STATES

UTILITY PATENT APPLICATION DECLARATION AND POWER OF ATTORNEY – ORIGINAL APPLICATION	ATTORNEY'S DOCKET NO.
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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name:

I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named below) of the invention entitled

(1) TITLE OF INVENTION (1) USE OF PHOTOCATALYTIC PREPARATIONS OF COLLOIDAL TITANIUM DIOXIDE FOR PRESERVING THE ORIGINAL APPEARANCE OF CEMENTITIOUS, STONE, OR MARBLE PRODUCTS

the specification of which

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(2) ☐ is attached hereto.

☒ was filed on Dec. 21, 2001 as Application No. 10/030,241

and was amended on July 26, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge my duty to disclose information of which I am aware which is material to the patentability of this application under 37 CFR 1.56(a): the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months prior to this application; and as to applications for patents or inventor's certificate on the invention filed in any country foreign to the United States prior to this application by me or my legal representatives or assigns.

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				Yes No
ALL FOREIGN APPLICATIONS, IF ANY, FILED MORE THAN 12 MONTHS PRIOR TO THIS APPLICATION				
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I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112. I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

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Power of Attorney: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Jeffrey A. Schwab, Registration Number 24,490  
 Thomas E. Spath, Registration Number 25,928  
 Jay S. Cinamon, Registration Number 24,156

Howard R. Jaeger, Registration Number 31,376  
 Anthony Coppola, Registration Number 41,493

Send correspondence to:  
**ABELMAN, FRAYNE & SCHWAB**  
 150 East 42<sup>nd</sup> Street  
 New York, New York 10017-5612

Direct telephone calls to:  
 Jeffrey A. Schwab, Thomas E. Spath,  
 Jay S. Cinamon, Howard R. Jaeger,  
 or Anthony Coppola at (212) 949-9022

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(6) DETAILS  
 REQUIRED  
 FOR EACH  
 INVENTOR

1-00	Full Name of Sole or First Inventor	Inventor's Signature	Date
	Rossano AMADELLI	<i>Rossano Amadelli</i>	Feb. 22, 02
	Residence Via Massarenti, 39 - Comune Voghiera - Fraz. Gualdo (FE) - ITALY ITX		Citizenship Italian
2-00	Post Office Address Università di Ferrara - Dpt. di Chimica - Via L. Bersari, 46 - Ferrara - ITALY		
	Full Name of Second Joint Inventor, If Any	Inventor's Signature	Date
	Luigi CASSAR	<i>Luigi Cassar</i>	Feb. 22, 02
3-00	Residence Via Europa, 42 - S. Donato Milanese - ITALY ITX		Citizenship Italian
	Post Office Address CTG Italcementi Group - Via Camozzi, 124 - Bergamo - ITALY		
	Full Name of Third Inventor, If Any	Inventor's Signature	Date
4-00	Carmine PEPE	<i>Carmine Pepe</i>	Feb. 22, 02
	Residence Via Casnidelli, 12 - Ponteranica (BG) - ITALY ITX		Citizenship Italian
	Post Office Address CTG Italcementi Group - Via Camozzi, 124 - Bergamo - ITALY		
5-00	Full Name of Fourth Joint Inventor, If Any	Inventor's Signature	Date
	Residence		Citizenship
	Post Office Address		
6-00	Full Name of Fifth Joint Inventor, If Any	Inventor's Signature	Date
	Residence		Citizenship
	Post Office Address		
7-00	Full Name of Sixth Joint Inventor, If Any	Inventor's Signature	Date
	Residence		Citizenship
	Post Office Address		
8-00	Full Name of Seventh Joint Inventor, If Any	Inventor's Signature	Date
	Residence		Citizenship
	Post Office Address		